

Similarities between electrochromic windows and thin film batteries

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Abstract

One of the most important type of electrochromic devices (smart windows) is essentially a transparent rechargeable thin film battery (rocking-chair type battery) consisting of a pair of complementary intercalation layers, separated by an ion-conducting polymer electrolyte and contacted by transparent conducting oxide electrodes on glass. At least one of that intercalation electrodes must show colouration by anodic oxidation or cathodic reduction. The similar features of electrochromics and rechargeable thin film batteries concern the material properties, structure of the layers, kinetics of switching (charge/discharge cycles), energy and power density and electrical parameters but also differences between them will be comprehensively discussed. Additionally, we have studied electrochromic devices containing WO_3 as cathodic and Prussian white (PW) as anodic electrochromic layers (glass/FTO/ WO_3/K^+ -Polymer/PW/FTO/glass). Such device configurations reaching high colouration efficiencies, especially in the near IR-range, with a long-term cycle stability $>10^5$ cycles. The optical response properties in relation to the current–time curves of the charge/discharge processes are discussed.

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1. Introduction

Electrochromic (“smart”) windows for the electrical modulation of the transmission and reflection of electromagnetic radiation (visible light and heat in the near infrared region) and rechargeable thin layer batteries have an unique application potential especially for new energy technologies and efficient use of energy in buildings [1]. The major function of electro-

chromic windows is to control the flow of light and heat passing the building glazing and the glazings of vehicles, trains, aircraft, spacecraft and ships [1–3]. The increasing demand for the use of rechargeable thin layer batteries concerns the storage of electrical energy with high energy and power density for mobile applications, especially for electrocars, telecommunication and other electrical devices [4,5]. Up to now, neither electrochromic devices nor rechargeable thin layer batteries have reached the necessary technical level in the direction of long-term stability and reliability, and low-cost production. Electrochromic devices and rechargeable thin layer batteries have a great deal in common, like the materials, chemical and

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structure requirements, physical–chemical operating mechanism and thin film deposition technologies [6]. These similar features were not enough explored in the past. The analysis of those features should stimulate further developments of both fields. The aim of this article is the investigation and discussion of some of those analogies.

2. Electrochemical reactions in electrochromic devices and batteries

There are presently three major electrochromic device configurations; battery-like, solution phase and hybrid structures [7]. The latter two types are the so-called self-erasing devices, in which one or both electrochromic substances are dissolved in a liquid or gel electrolyte, where they can freely diffuse. That devices have been used in commercial electrochromic mirrors, but they do not have open circuit memory, requiring a continuous current injection to maintain the device in a coloured state. These are not favorable properties for use in switchable glazings for buildings and vehicles.

In the battery-like electrochromic devices as shown in Fig. 1, complementary thin film intercalation layers (EC_1 and EC_2) among which at least one must show colouration by anodic oxidation or cathodic reduction, coat the optically transparent electrodes (TCO). An

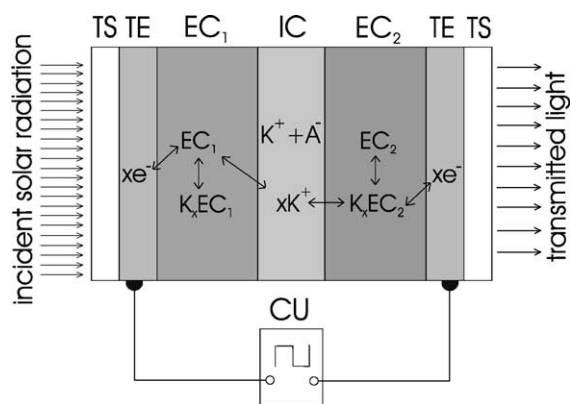
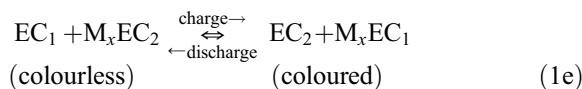
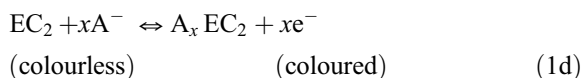
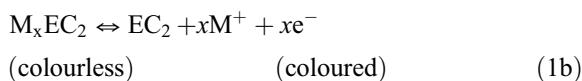
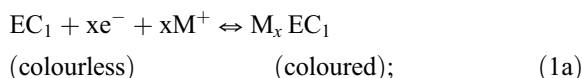


Fig. 1. Electrochemical reactions, electron and ion exchange processes in an electrochromic device (TCO: transparent conducting electrodes, IC: ion conducting polymer film with KA: dissolved salt, EC_1 and EC_2 : complementary intercalation layers, one or both have to be electrochromic layers, CU: control unit).

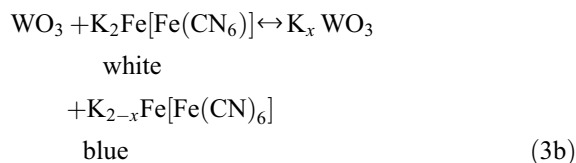
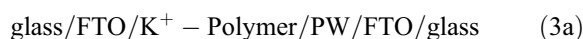
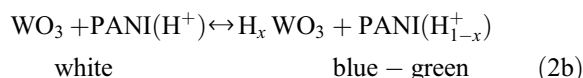
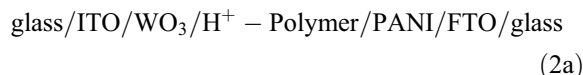
ion-conducting, electronically insulating electrolyte (IC) which may be a polymer/gel electrolyte separates the electrochromic layers EC_1 and EC_2 . Polymer or gel electrolytes lead to a laminated sandwich structure, which one can often find among the thin film batteries too. Such electrochromic devices show an extended open circuit memory similar to thin film batteries.

Fig. 1 schematically shows the electrochemical reactions, the electron and ion exchange and motion through the device, leading to the colouration or bleaching and in this way to the control of the electromagnetic radiation. The corresponding chemical Eqs. (1a)–(1b) show the mass and charge balance. M^+ denotes the protons and other cations (Li^+ , Na^+ , K^+) and A^- denotes the anions. x is the intercalation coefficient (insertion coefficient).

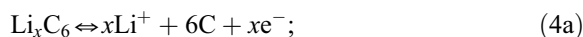


In most electrochromic devices, the electrochemical reactions in the intercalation electrodes corresponds to Eqs. (1a) and (1b) leading to the overall reaction (1e). During the charging of the electrochromic device resulting in colouration, the cathodic reduction of EC_1 (Eq. (1a)) takes place with the intercalation (insertion) of xM^+ and the anodic oxidation of $M_x EC_2$ (Eq. (1b)) with the exsersion of xM^+ . An electrochromic device with two electrochromic half cells corresponding to Eqs. (1a) and (1b) is a so-called complementary electrochromic window. The electrochromic devices studied in this paper uses WO_3 as cathodic and either polyaniline (PANI) [8] or Prussian white (PW) as anodic electrochromic half cells with device configurations and

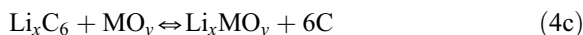
overall reactions corresponding to Eqs. (2a,2b) and (3a,3b).



Most of the materials used in rechargeable thin film batteries are intercalation compounds with Li^+ [4,9]. The host materials may be an oxide or sulphide of Ti, Mn, Co, V but also graphite or other modifications of carbon. The electrochemical reactions within the half cells with Li-graphite intercalation compound LiC_6 and a metal oxide (MO_y) are shown in Eqs. (4a) and (4b), the charge/discharge cycles of the overall reaction in Eq. (4c) [10,11].



charge/discharge cycles :



The examples of intercalation reactions in electrochromic devices Eqs. (2a,2b) and (3a,3b) and rechargeable thin film (swing) batteries involve a transfer of small and high mobile cations (Li^+ , K^+ and H^+) during the colouring/bleaching or charge/discharge cycles. In the same way, the intercalation of anions (A^-) corresponding to Eq. (1d) accompanied by the dissociation reaction Eq. (1c) is also a practical way of the operation of electrochromic devices and swing batteries. This configuration occurs mainly in devices and batteries where one of the half cells is an electronic conducting polymer (polypyrrole, polythiophene), since the colouration occurs during the anodic oxidation [12]. In this case, the resulting positive charge within the

polymer layer must be compensated by an anion (A^-), whose transfer is the rate limiting step and its velocity is much smaller than the cation transfer.

The principal electrical and optical response properties in dependence on square wave voltage pulses are discussed in relation to current–time behavior (Fig. 2). Fig. 2 shows the storage properties of optical (upper curves) and electrical properties (middle curves) under the influence of square wave voltage pulses (under region of Fig. 2). This figure displays the storage of the electrical charge capacity (middle curves) as well as the optical darkening (upper curves in Fig. 2). This picture (Fig. 2) shows clearly that the electrical properties (charge and discharge properties) of an electrochromic device correspond to those of a battery. An electrochromic device is a rechargeable thin film battery with transparent electrodes. Peaks in the charging curves (I vs. t plot in Fig. 2) represent the insulator/metal transition (percolation threshold), resulting from the occupation of d-conduction bands of M_xWO_3 or soliton levels (Π -levels) in electronic conducting polymers [6,8]. We have observed this switch behavior at earlier investigations on electrochromic devices with WO_3 and PANI (Eqs. (2a) and (2b)), as complementary electrochromic layers [6]. For some electrochromic devices, the bleaching velocity is faster than the colouring velocity, because the coloured nearly metallic conducting state of the electrochromic layer presents an electronic conductivity much higher than that of bleached state. A detailed discussion of switching properties of electrochromic devices with WO_3 and Prussian white (Figs. 5, 6 and 7) than complementary electrochromic layers and

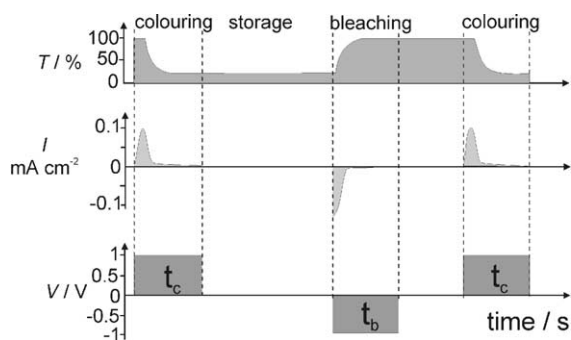


Fig. 2. Electrical and optical switching behavior of an electrochromic device in response to rectangular voltage pulses (t_b ...bleaching time, t_c ...colouring time).

resulting conclusions of kinetics and mechanism is given in the last chapter.

Although many analogies exist in regard to the mechanism of the energy supplying processes in rechargeable thin layer batteries and electrochromics, for example, to the charge and discharge mechanisms corresponding to reactions (1a)–(1e), they also exhibit some differences. A survey of analogous features and of differences in direction of the requirements on properties of the used thin film materials and switch behavior is provided in Table 1.

One of the most important operating parameter of an electrochromic device or an electrochromic substance is the *colouration efficiency* CE (Eq. (5)).

$$CE = \Delta OD/Q = \Delta[\log(T_0/T)]/Q \text{ [cm}^2/\text{C}] \quad (5)$$

T_0 is the transmittance of the electromagnetic radiation in the bleached state of the window and T is the transmission after the flow of the electrical charge Q through the device. The colouration efficiency and the optical density depend on the wavelength and are usually higher in the near IR than in the visible region. By use of complementary electrochromic devices from types (2a) and (3a), it is easy to

achieve CE values about $150 \text{ cm}^2/\text{As}$ in the visible region (see Table 1 and Fig. 4).

Using Ohm's law ($U_S = RI = RQ/t_S$) with the switch voltage U_S , the resistance R and the surface area A , together with Eq. (5), an estimate value of the switching time t_S is:

$$t_S = Q \cdot R/U_S = \Delta OD \cdot A \cdot R/(CE \cdot U_S) \quad (6)$$

Taking $\Delta OD = 1$, $CE = 150 \text{ cm}^2/\text{As}$, $U_S = 1.5 \text{ V}$, and $R = 10 \text{ } \Omega$, the switching time is 0.9 s for an electrochromic device exhibiting an active surface of 1 cm^2 and 900 s for an electrochromic window with $A = 1 \text{ m}^2$. This is a rough approximation without consideration of the resistances of electrolyte and of electrochromic layer.

3. The complementary electrochromic Prussian blue/tungsten oxide system

Films of Prussian blue (PB) and WO_3 have been obtained by galvanostatic electrodeposition [8,13,14] on transparent electrodes consisting of fluorine-doped tin dioxide, $\text{SnO}_2:\text{F}$ (FTO), with a sheet resistance of

Table 1

Comparison of essential operating features and requirements for electrochromic windows and rechargeable thin film batteries

Characteristic, requirements	Electrochromic window	Rechargeable thin layer battery
Energy and charge density	low, the essential characteristic is the colouration efficiency, $CE = \Delta(OD)/Q > 150 \text{ cm}^2/\text{As}$ is desired	high energy and charge density are required $> 100 \text{ W h}/(\text{kg})$
Open circuit voltage, V_O	as low as possible, $V_O < 1 \text{ V}$, a high V_O leads to decrease of the cycling life time	V_O should be high $\sim 2\text{--}3 \text{ V}$ for the single cell, 4 V can be achieved without importance
Optical properties	high contrast ratio also in the near IR, different colour tinting	
Porosity	very disadvantageous, leads to scattering and clouding	advantage for the intercalation properties, leads to increasing energy and power density
Speed of charge and discharge	should be high, high diffusion coefficient and migration rate lead to increase of switching rate	should be high, lead to increase of power density
Cycle life	cycle number $> 10^5$ cycles	should be high but often < 1000 cycles
Electronic conductivity, μ	should be high and constant in both cases, μ depends on the degree of intercalation, therefore, μ changes during the switches	
Polymer or gel electrolyte	no electronic and high ionic conductivity ($10^{-3}\text{--}10^{-4} \text{ S cm}^{-1}$), transparent and with a good adhesion on glass, flexible	no electronic and high ionic conductivity, so far as possible $< 10^{-3} \text{ S cm}^{-1}$, stringent nonaqueous
Discharge depth	a deep discharge is necessary to achieve a high transmittance in the bleached state	deep discharge must be avoided, leads often to decrease of the life time, irreversible changes of the structure of the host substances
Collector electrodes	must be transparent, for electrochromic windows $\text{SnO}_2:\text{F}$ (FTO) is preferred, problem: the high sheet resistance ($\sim 18 \text{ } \Omega/\square$), for structured devices (displays) $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) is used	use of graphite or special carbon electrodes which exhibit a good electronic conductivity

and bleaching cycles, for several switching voltages. The comparison of the current–time curves of charge and discharge revealed that the charge process is slower than the discharge. During charging, a continuous decrease in the current densities with the time occurs, whereas the discharge process presents turning points. The higher rate of discharging results from higher electronic conductivity of the electrochromic layers in the charged state. In addition, the process of charging is accompanied by the development of a back *emf* which delays [15]. On the other hand, the discharge is a spontaneous reaction which also occurs as a short-circuit reaction.

A mathematical simulation of the charge curves (see Fig. 7) demonstrates that the charge is not a simple diffusion-controlled intercalation reaction, following a $t^{-1/2}$ relation, but it shows an additional voltage dependence because migration is present [8]. In such a case, the $I-t$ response should be more steeply decreasing. The best simulation of the experimentally $I-t$ response has been found with a superposition of a $t^{-1/2}$ relation with an $\exp(-t)$ relation, corresponding to Eq. (9), as shown in Fig. 7.

$$I = \frac{A}{\sqrt{t}} B \exp(V_S) + \frac{V}{R} \exp\left(-\frac{t}{RC}\right) \quad (9)$$

The second term in Eq. (9) corresponds to a capacitor-like behavior of the electroactive electro-

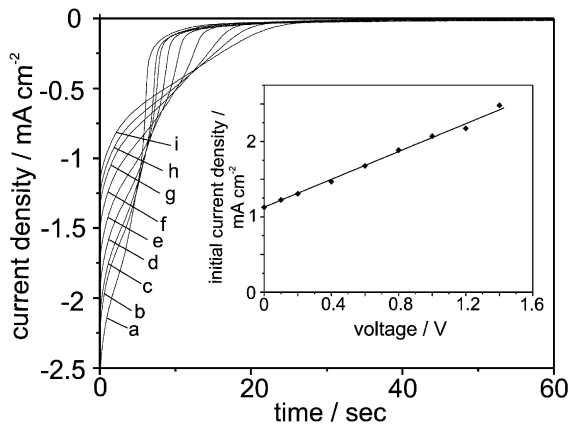


Fig. 6. Current density vs. time curves for the discharge (bleaching) of an electrochromic device shown in Fig. 4 for different switching voltages V_S . Values for V_S : (a) -1.4 V, (b) -1.2 V, (c) -1.0 V, (d) -0.8 V, (e) -0.6 V, (f) -0.4 V, (g) -0.2 V, (h) -0.1 V, (i) 0 V. The inserted figure shows the dependence of the initial discharge current on the switching voltage.

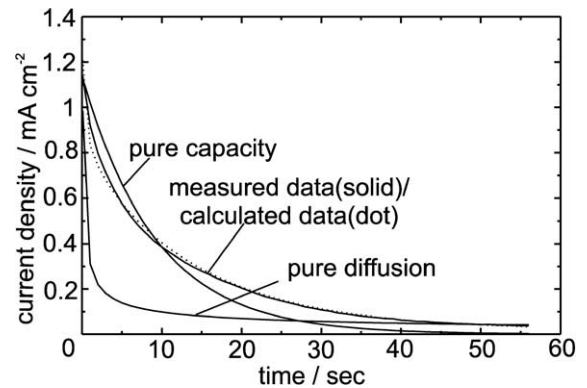


Fig. 7. Experimental and simulated charging curves. The simulation was performed for a diffusion/migration-controlled mechanism, for a capacitor-like and for a superimposition of diffusion and capacitor-like behavior process in correspondence to Eq. (9). Charging voltage: 1.4 V.

chromic layers where C is a pseudo capacitance which one can find in electrochemical supercapacitors [16].

It is also important to point out that the initial current densities exhibit a linear dependence on the switching voltage, for both the charge and the discharge (see the insets within Figs. 5 and 6).

4. Conclusion

The most important type of electrochromic devices is a battery-like window, essentially a transparent rechargeable thin film battery (rocking-chair type) consisting of a pair of complementary intercalation layers, separated by an ion-conducting polymer electrolyte and contacted by transparent conducting oxide electrodes on glass. At least one of that intercalation electrodes must show colouration by anodic oxidation or cathodic reduction. The similar features of electrochromics and rechargeable thin film batteries concern the material properties (intercalation capability), structure of the layers, kinetics and mechanism of switching (charge/discharge cycles), energy and power density, extended open circuit memory and other electrochemical parameters, for example, a high exchange current density. High electron transfer rates between collector electrodes and active layers, a good electron and ion conductivity within in the active layers and high ion conductivity of the polymer electrolyte present much analogous features too.

Essential differences between electrochromic devices and thin film batteries concern the charge density in relation to the efficiency, the open circuit voltage V_O , the requirements in regard to porosity, the cycling life time, the discharge depth and the electrical and optical properties of collector electrodes and active layers.

A viable electrochromic smart window must for example exhibit a cycling life time $>10^5$ cycles corresponding to an operation life at 10–20 years. In comparison, the cycle lifetime of the batteries is often <1000 cycles. A stringent requirement concerns the charge and discharge depth of electrochromic devices. These must be very deep to achieve a high range for the change of optical density, a high transmittance in the bleached state and low transmittance in the darkened state. For batteries, an overload and a deep discharge is bad and must be avoided, since that often leads to the decrease of cycle life and irreversible changes of the structure of the host substances.

Compared to batteries, the requirements of charge densities for electrochromic windows are quite severe, too. A high colouration efficiency (5) and a high speed of the switching cycles require a low charge density for a high response in the optical density. Batteries must show a high charge density. On the

other hand, the electrochromics must exhibit a low open circuit voltage ($V_O < 1,2$ V) but V_O should be >2 V for batteries.

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